



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Modelling Thermodynamics of Alloys for Fusion Application

A. Caro, B. Sadigh, P. E. A. Turchi, M. Caro, E. Lopasso, D. Crowson

January 26, 2006

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

MODELLING THERMODYNAMICS OF ALLOYS FOR FUSION APPLICATION - A. Caro, B. Sadigh, P. E. A. Turchi, and M. Caro, (Lawrence Livermore National Laboratory), E. Lopasso (Centro Atomico Bariloche, Argentine), and D. Crowson (Virginia Polytechnical Institute)

OBJECTIVE

This research has two main objectives.

- On one side is the development of computational tools to evaluate alloy properties, using the information contained in thermodynamic functions to improve the ability of classic potentials to account for complex alloy behavior.
- On the other hand, to apply the tools so developed to predict properties of alloys under irradiation.

SUMMARY

Atomistic simulations of alloys at the empirical level face the challenge of correctly modeling basic thermodynamic properties. In this work we develop a methodology to generalize many-body classic potentials to incorporate complex formation energy curves. Application to Fe-Cr allows us to predict the implications of the *ab initio* results of formation energy on the phase diagram of this alloy.

PROGRESS AND STATUS

We address the problem of alloy description with atomistic models from the perspective of thermodynamics. We derive the phase diagram of a model Hamiltonian, namely, the embedded-atom EAM potential for Fe-Cr.

To do so, we follow the procedure described in [1-2] and apply it to Iron alloys with different Chromium concentrations. The same computational thermodynamics tools developed in [3] were applied with success in the case of Fe-Cu alloys to predict the phase diagram of such a system.

Gibbs free energies for the solid and liquid phases are calculated using MD simulations for pure elements and for several Fe-Cr alloys. In this work, we use the Fe potential reported in [4] and the Cr potential reported in [5]. For the cross potential we use the methodology described in [6] that incorporates the complex formation energy curve for Fe-Cr. The cross potential is derived so that it reproduces the calculated *ab initio* formation energy Δh of Olsson et al. [7]. The formation energy of bcc ferromagnetic Fe-Cr alloys given in [7] can be reproduced by a Redlich-Kister expansion to 4th order in $(1-2x)$ as follows:

$$\Delta h = x(1-x) \sum_0^n L_p (1-2x)^p \quad (1)$$

As we see in Fig.1 Δh is highly non-symmetric and even changes sign at low Cr composition.

Phase Diagram of the Fe-Cr Empirical Potential

We calculate the free energy per particle at a given temperature T , $f(T)$, through thermodynamic integration between the state of interest and a reference state at temperature T_0 with known free energy $f(T_0)$. The free energy per particle is given by the Gibbs-Duhem integral:

$$f(T) = f(T_0) \frac{T}{T_0} - T \int_{T_0}^T \frac{h(t)}{t^2} dt \quad (2)$$

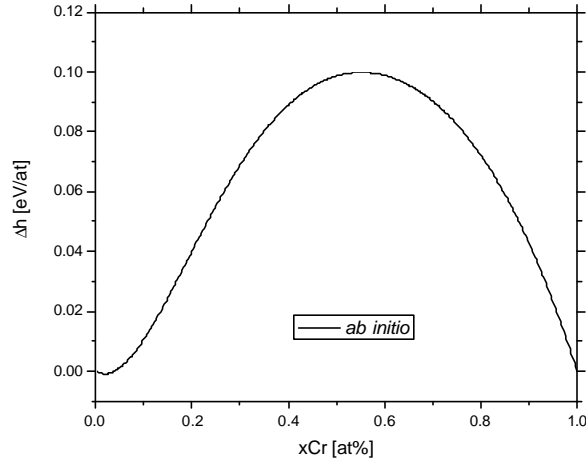


Fig. 1: Calculated mixing enthalpy for ferromagnetic bcc Fe-Cr alloys, corresponding to Fe-Cr in the low temperature range ($T < 1000$ K)

Second-order polynomials are adjusted to the simulation results of the internal enthalpy for solid and liquid Fe-Cr alloys, and the integral of Eq. (2) is solved analytically.

The resulting Gibbs free energies and enthalpy per particle are computed as:

$$\begin{aligned} g(T) &= A + B T + C T^2 + D T \ln(T) \\ h(T) &= A + 2DT + CT^2 \end{aligned} \quad (3)$$

We can also express the free energy of a random solid solution phase of an alloy with composition x at temperature T as:

$$g(x, T) = g_{\text{ref}}(x, T) + g_{\text{mix}}(x, T) + Dg(x, T) \quad (4)$$

where g_{ref} , g_{mix} are given by (k is Boltzmann constant equal to 8.617385×10^{-5} eV/K):

$$\begin{aligned} g_{\text{ref}}(x, T) &= (1-x) g_{\text{Cr}}(T) + x g_{\text{Fe}}(T) \\ g_{\text{mix}}(x, T) &= kT [(1-x) \ln(1-x) + x \ln(x)] \end{aligned}$$

The excess Gibbs energy of mixing can also be conveniently expressed by a Redlich-Kister expansion [8] as:

$$\Delta g(x, T) = x(1-x) \sum_{p=0}^n L_p(T) (1-2x)^p \quad (5)$$

where $L_p(T)$ is the p th-order binary interaction parameter.

Bearing Eqs. (4-5) in mind we choose to express the functional form of each coefficient A , B , C , and D in Eq.(3) as:

$$\text{Coeff} = C_{\text{Fe}} (1-x) + C_{\text{Cr}} x + x (1-x) S L_p^{\text{Coeff}} (1-2x)^p$$

With these values we build up a database for Fe-Cr and use the software package Thermo-Calc [8] to calculate the phase diagram shown in Fig. 2.

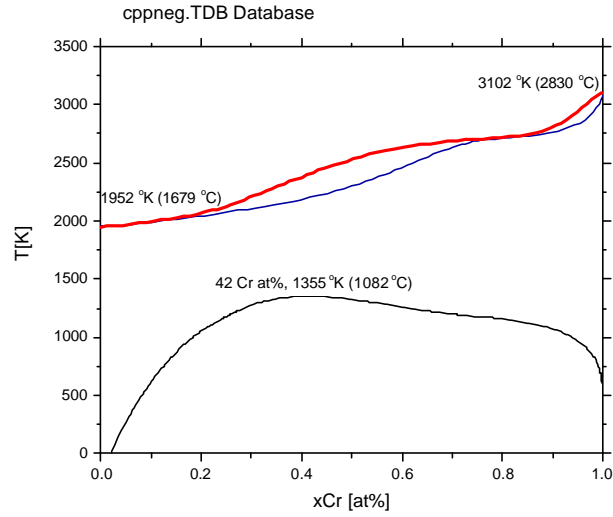


Fig. 2: Predicted phase diagram obtained from the application of the Thermo-Calc software to the database *cppneg.TDB* generated using the Fe-Cr empirical potential.

The Heat of Formation

Experimental points have been reported at $T = 1600\text{ K}$. The SSOL library in Thermo-Calc (CALPHAD) package reproduces these points very well.

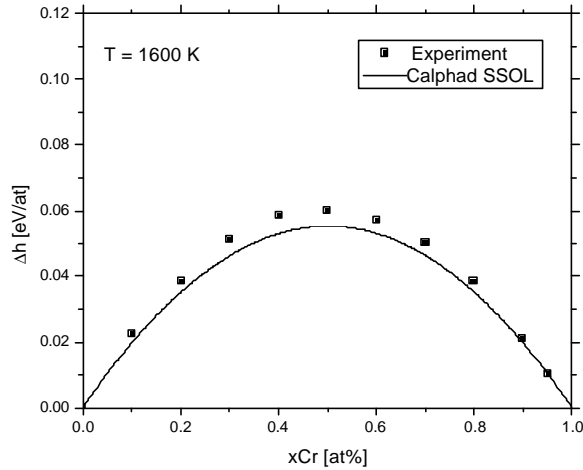


Fig. 3: Heats of formation of Fe-Cr as described in the database of Calphad and experimental measurements..

Our database *cppneg.TDB* based on the Fe-Cr empirical potential reproduces well the calculated *ab initio* formation energy at low temperature.

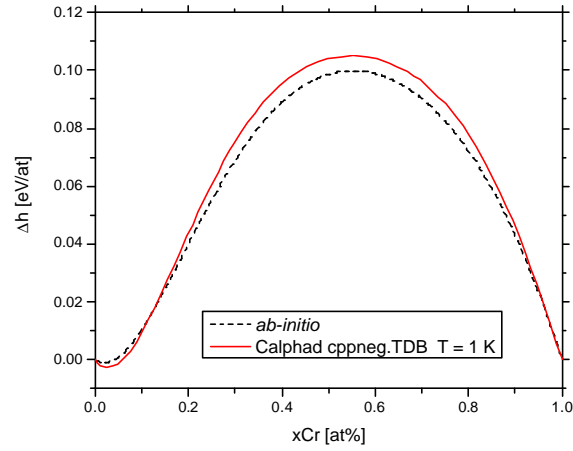


Fig. 4: Heats of formation of Fe-Cr as described in the database built upon our potential and the *ab initio* results.

The point of controversy is the difference in the formation enthalpy of the ferromagnetic solid solution between *ab initio* calculations and CALPHAD SSOL, see graph below:

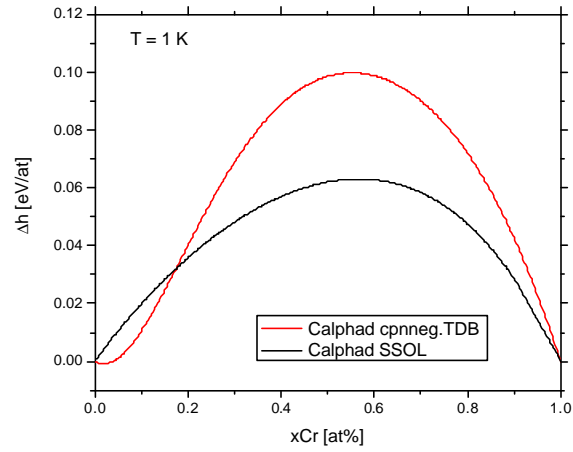


Fig. 5: Heats of formation of Fe-Cr as described in the database of Calphad and our own based on the *ab initio* results.

The Entropy calculated for the classic potential appears to be remarkable close to the Calphad values indicating a good over-all reproduction of the dynamics of the system.

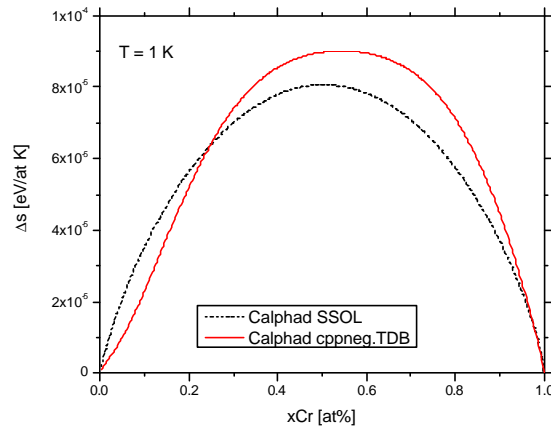


Fig. 6: Entropy of formation of Fe-Cr as described in the database of Calphad and our own database based on *ab initio* results.

Comparison with the Experimental (CALPHAD) Phase Diagram

The experimental phase diagram is obtained using the SSOL library in Thermo-Calc. Melting points are shown in the table below:

	Fe	Cr
SSOL	1810 K (1537 °C)	2180 K (1907 °C)
Cppneg.TDB	1952 K (1679 °C)	3102 K (2830 °C)

Pure Cr is poorly described, as its melting point is significantly above the experimental value. The phase diagram obtained using Thermo-Calc appears in the graph below. Note that BCC, FCC, Sigma and Liquid phases of the SSOL database are included.

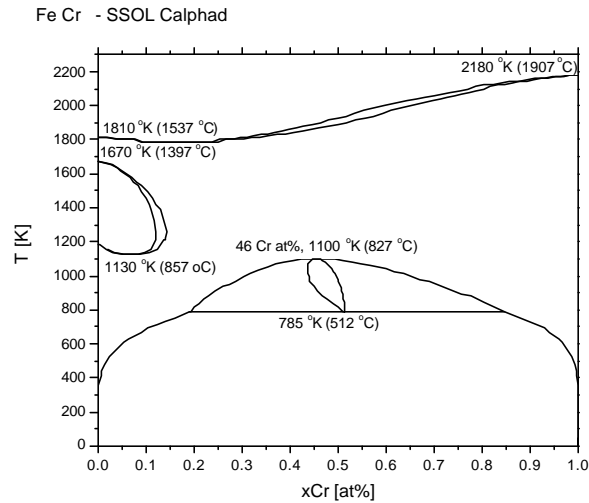


Fig. 7: Experimental phase diagram of the Fe-Cr system.

Neglecting all phases but Liquid and BCC, we obtain the phase diagram shown below .

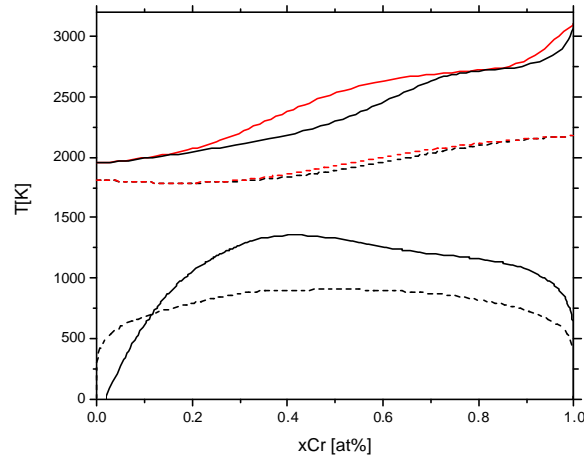


Fig. 7: Phase diagram reporting only liquid and bcc phase of the Fe-Cr system as measured experimentally (dotted lines) and as implied by the ab initio results (solid lines)

Solid lines correspond to the results obtained in this work. Dash lines correspond to SSOL CALPHAD database. The “experimental” (CALPHAD) miscibility gap has a maximum at 904.7 K ($x_{Cr} \sim 0.515$ at%) and is quite symmetric as compared to the highly nonsymmetrical miscibility gap is found in our work. The miscibility gap has a different shape at low concentration, the solid curve goes to zero at $x_{Cr} = 0.0197$ at%.

These results prove on one side the ability of our approach to go from ab initio results to classic potentials, and to go from classic potentials to thermodynamics. From here on, we can reliably use the potentials so developed to evaluate non equilibrium processes induced by radiation.

References

- [1] E. Ogando Arregui, M. Caro, and A. Caro, “Numerical evaluation of the exact phase diagram of an empirical Hamiltonian: Embedded atom model for the Au-Ni system”, *Phys. Rev. B* 66 (2002) 054201.
- [2] E. M. Lopasso, M. Caro, A. Caro, and P. E. A. Turchi, “Phase diagram of an empirical potential: The case of Fe-Cu”, *Phys. Rev. B* 68 (2003) 214205
- [3] A. Caro, P. E. A. Turchi, M. Caro, E. M. Lopasso, “Thermodynamics of an empirical potential description of Fe-Cu alloys”, *J. Nucl. Mater.* 336 (2005) 233-242.
- [4] M. I. Mendelev, S. Han, D. J. Srolovitz, G. J. Ackland, D. Y. Sun, and M. Asta, *Phil. Mag.* 83 (2003) 3977.
- [5] J. Wallenius, P. Olsson, C. Lagerstedt, N. Sandberg, R. Chakarova, and V. Pontikis, *Phys. Rev. B* 69 (2004) 094103.
- [6] A. Caro, D. A. Crowson, and M. Caro, “Classical many-body potential for concentrated alloys and the inversion of order in iron-chromium alloys”, *Phys. Rev. Lett.* 95 (2005) 075702.
- [7] P. Olsson, I. A. Abrikosov, L. Vitos, J. Wallenius, “Ab initio formation energies of Fe-Cr alloys”, *J. Nucl. Mater.* 321 (2003) 84-90

[8] N. Saunders and A. P. Miodownik, CALPHAD: A comprehensive guide, edited by R. W. Cahn, Pergamon Materials Series (Oxford, New York, 1998).

[9] N. Saunders and A. P. Miodownik, *Calphad. A comprehensive guide* (Pergamon Materials Series, R. W. Cahn Editor, 1998).

[10] Tables with the potential are available upon request to the authors.

[11] I. Mirebeau, M. Hennion, and G. Parette, Phys. Rev. Lett. 53, 687 (1984).

[12] M. Hennion, J. Phys. F. 13, 2351 (1983).

Publications

[1] Caro, M., Lopasso, E. M., Turchi, P. E. A., Farkas, D., "Thermodynamics of Fe-Cu Alloys as Described by the Ludwig - Farkas EAM Potencial," In press, Journal of Nuclear Materials 2006.

[2] Crowson, D., and Caro, M., "Classic many body potential for concentrated alloys," Phys. Rev. Lett. 95 (7), 075702 (2005).

[3] L. A. Zepeda-Ruiz, G. H. Gilmer, B. Sadigh, A. Caro, and T. Oppelstrup. "Atomistic simulations of grain boundary pinning in CuFe alloys". APPLIED PHYSICS LETTERS 87 (23): Art. No. 231904 DEC 5 2005.

[4] J. Marian, A. Caro. "Moving dislocations in disordered alloys". Submitted.

[5] A. Caro, E. M. Lopasso, M. Caro. Implications of *ab initio* energetics on the Fe-Cr thermodynamics. In preparation